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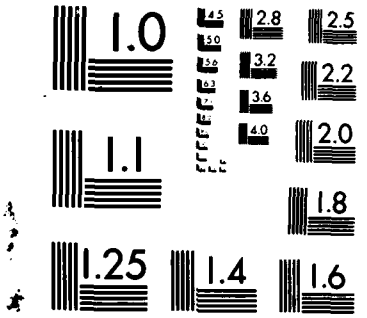

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CHLORIDE IN CLEANING COMPOUNDS

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Military specification, MIL-C-85704, requires the screening of turbine engine compressor cleaning compounds (or gas path cleaners) for their chloride content. The chloride concentration should not exceed 100mg/L. A direct method for chloride analysis in various cleaning compounds has been developed.

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INTRODUCTION

Elemental analysis of candidate turbine engine compressor cleaning compounds is required to screen high levels of chloride content. A variety of wet chemical, extraction and ion specific electrode methods are available for the determination of chloride.[1-7] Because of the complex formulation of the cleaning compounds, these methods require sample preparation by acid or Parr bomb digestion. The sample preparation process is tedious and time consuming, and can create interferences. A direct micro-coulometric titration method for chloride in cleaning compounds has been used successfully. This method does not require sample preparation.

In this method, an electrochemical titration cell containing a silver-silver acetate electrode system responds to any substrate which can react with the silver ions. The chloride standard solution and samples in microliter quantities are pyrolysed and their oxidation products are carried to the titration cell by a carrier gas, where coulometric titration takes place. The amount of chloride present in the solutions is displayed in mg/L on the micro-coulometer.

EXPERIMENTAL PROCEDURE

Materials required to perform the micro-coulometric titration analysis are listed in Table 1. The instrument used was a Dohrmann-Xertex Micro-Coulometric Titration System (MCTS-20) and its setup parameters are described in Table 2. The experimental procedure was established by performing analyses on known chloride containing organic compounds.

The titration cell used was a T-300-S (Dohrmann-Xertex) and its setup was critical for the chloride analysis. The cell cap was placed on the cell in a way that the two electrodes (sensor and working) were parallel to the gas flow from the pyrolysis furnace. The electrolyte level was maintained at about 1/2" above the electrodes. A gentle tap on the cell arm and opening the drain stopcock helped in removing any trapped air bubbles in the cell. The electrolyte was changed every four hours and stirred continuously at a constant speed during analysis. When the cell was not in use, it remained filled with the electrolyte solution. Yellow or brown spots on the electrodes caused erratic results and an unstable baseline. Electrodes were removed from the cell, cleaned and plated electrolytically for 8 or more hours.

Once the cell was setup, it was connected to the pyrolysis furnace and allowed to equilibrate to a steady-rate negative (-2.0) baseline value. A (-) polarity value indicated that the titrant ions were being generated and a (+) polarity indicated that the titrant ions were being removed. If the baseline value was positive, the cell was flushed with fresh electrolyte solution.

The instrument calibration and accuracy of analysis depended on the correct volume of standard or sample injection. A 5μL sample solution was injected into the furnace at a constant rate of 0.2μL to 1μL per second. Standard chloride solutions prepared in the laboratory were used for the calibration of the equipment. Samples (as received and diluted with ethanol) were analyzed after the calibration under the same experimental conditions. Whenever the cell electrolyte was changed or the percent recovery was below 70%, MCTS was recalibrated.

RESULTS

When a sample solution is pyrolysed at 800-1100°C in the presence of an oxidant, its possible oxidation products are:

$$\text{Carbon} \longrightarrow CO_2$$
$$\text{Sulfur} \longrightarrow SO_2 + SO_3$$

Hydrogen $\longrightarrow H_2O$
Phosphorus $\longrightarrow P_2O_5$
Nitrogen $\longrightarrow NO_x$
Halogens (C. ..ide) $\longrightarrow X_2 + HX + HOX$ (Cl_2 + HCl + HOCl)

Only the chlorine products have the capability of generating a positive response in the silver-silver acetate electrolde system:

$$Cl_2 + HCl + HOCl + 4Ag^+ \longrightarrow 4AgCl\downarrow + H_2O$$

Four organic compounds, chlorobenzene, methylene chloride, trichloroethane and trichloroethylene were analyzed for their chloride content. Results for various concentrations of the recovered chloride are reported in Table 3. A ±5.0 percent error was found for 2 parts per million (ppm) concentration of chloride.

Since sulfur has a strong affinity towards silver, the tolerance of sulfur concentrations for chloride analysis was also investigated. Solutions were prepared with a known concentration of chloride and sulfur in 1:4, 1:8, 1:20, 1:40 and 1:50 ratio. By analyzing these solutions, it was established that the presence of sulfur in 1:40 ratio does allow the determination of 50mg/L chloride with +8.0% error. Sulfur in 1:50 ratio created 30% error, but the results obtained were not consistent. Results of sulfur tolerance for chloride analysis are reported in Table 4.

The three cleaning compounds studied were B&B 3100, Penair M-5704 and Rochem. These compounds were analyzed without any sample preparation. Dilution of these samples were made with ethanol. Blank runs for the solvent ethanol were made for any trace amount of chloride. Blank corrections were applied to all the sample chloride values. Results for the analyses of the three cleaning compounds with and without dilution are presented in Table 5.

Ion selective electrode and ion chromatography methods were also applied to these cleaning compounds. Both methods require aqueous sample solutions. Acid digestion with sulfuric and nitric acid mixtures and a Parr bomb digestion method were used to prepare the sample solutions. A direct micro-coulometric titration, where sample was not pyrolysed but injected directly to the electrochemical cell was also used for aqueous cleaning compound sample solutions. Comparative data for various methods used for the chloride determination are presented in Table 6. Chloride values reported in Tables 3 thru 6 are an average of 20-30 analysis runs.

LIMITATIONS

1. Any material that can react with silver ions interferes positively.

2. This method does not work when the chloride and sulfur ratio is 1:50 or higher.

3. Incomplete combustion in the pyrolysis furnace results in interferences due to the formation of sulfides, cyanides and acetylene.

4. High sodium content of a sample attacks the pyrolysis tube and thus shortens the tube life. Samples, if prepared by Parr bomb digestion, should be passed thru an ion exchange column before analysis.

CONCLUSIONS

Results reported in Tables 3-6 confirm that the micro-coulometric titration method can be successfully used for total chloride content in samples of complex organic matrix. This method is time efficient, cost effective and reproducible.

Future work will involve the determination of chloride below 1 parts per million concentration. A single boat inlet (SBI) accessory will be used to study highly viscous and low chloride content samples.

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The author expresses her thanks to K. Clark and M. Cannon, Naval Air Development Center, J. Callaghan, Villanova University and J. Martin, Dohrmann-Xertex for their assistance in the development of this method. Any mention of trade name of a product or its manufacturer should not be construed as its endorsement.

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TABLE 1. MATERIALS REQUIRED

Electrodes	Platinum electrodes 4 (sensor, reference and 2 working electrodes plated with silver).
Plating equipment	Electroplating unit, magnetic stirrer and bars.
Plating solution	A mixture of 4g AgCN, 4g KCN and 6g K_2CO_3 in 100 ml of distilled water.
Electrolyte	70% (v/v) acetic acid/water.
Standard chloride solution	Chlorobenzene in iso-octane
Blank solution	iso-octane or the solvent used for sample preparation.
Syringe	10 μL with an automatic dispenser.
Oxygen gas	Ultra high pure
Carrier gas	Argon or helium, 99.95% pure.
Samples	Used as received or diluted with a proper solvent.

TABLE 2. INSTRUMENT PARAMETERS

FURNACE TEMPERATURE SETTINGS:

Inlet	700°C
Center	800°C
Outlet	800°C

GAS SETTINGS:

Reactant gas (O_2)	160 ml/min.
Carrier gas (He/Ar)	40 ml/min.

COULOMETER SETTINGS:

Single Cycle Operate	ON
Bias	250 mV
Gain	1100-1200
Time	300 secs. (adjustable)
Element Integrate Range	Cl X 1 (adjusted as required).

TABLE 3. ANALYSIS OF KNOWN ORGANIC COMPOUNDS FOR CHLORIDE

NAME	CHLORIDE mg/L		ERROR (%)
	Taken	Found	
Chlorobenzene	498.3	490.0	-1.66
	199.8	196.4	-1.70
	39.8	38.6	-3.0
	25.1	25.5	±1.8
	10.0	9.8	-2.0
	5.0	4.9	-2.0
	2.0	2.1	+5.0
Methylene Chloride	50.4	49.3	-2.2
	25.0	27.4	+9.6
	5.0	4.9	-2.0
Trichloroethane	50.0	52.4	+4.8
	25.1	26.5	+5.6
	5.0	4.86	-2.8
Trichloroethylene	25.0	24.98	-0.8
	5.0	4.95	-3.0

TABLE 4. CHLORIDE IN THE PRESENCE OF SULFUR

Chloride and Sulfur Ratio	CHLORIDE IN mg/L		ERROR (%)
	Taken	Found	
1:4	50.4	51.3	+1.8
1:8	50.3	50.75	+0.9
1:20	50.1	50.8	+1.39
1:40	50.0	54.0	+8.0

TABLE 5. FURNACE INJECTION OF CLEANING COMPOUNDS

Sample	Total Chloride [mg/L]	Standard Deviation
B & B 3100	16.6	1.19
B & B 3100 (2 x dilution with ethanol)	16.3	0.76
B & B 3100 (10 x dilution with ethanol)	17.0	0.48
Penair	26.3	0.11
Penair (2 x dilution with ethanol)	25.0	0.33
Penair (10 x dilution with ethanol)	24.0	0.57
Rochem	61.1	2.57
Rochem (2 x dilution with ethanol)	63.0	0.42
Rochem (10 x dilution with ethanol)	61.0	0.52

TABLE 6. COMPARATIVE DATA FOR CHLORIDE IN CLEANING COMPOUNDS

	Analytical Method Used	ROCHEM mg/L	PENAIR mg/L	B&B 3100 mg/L
1.	Direct furnace injection micro-coulometric titration. No sample preparation.	61.7	25.1	16.63
2.	Direct micro-coulometric titration after Parr bomb injection.	63.0	25.5	25.0
3.	Ion selective electrode method after Parr bomb digestion.	65.0	24.0	14.9
4.	Ion chromatography after Parr bomb digestion.	60.0	26.0	20.7
5.	Furnace injection micro-coulometric titration method after Parr bomb digestion and ion exchange treatment.	62.6	27.3	17.5

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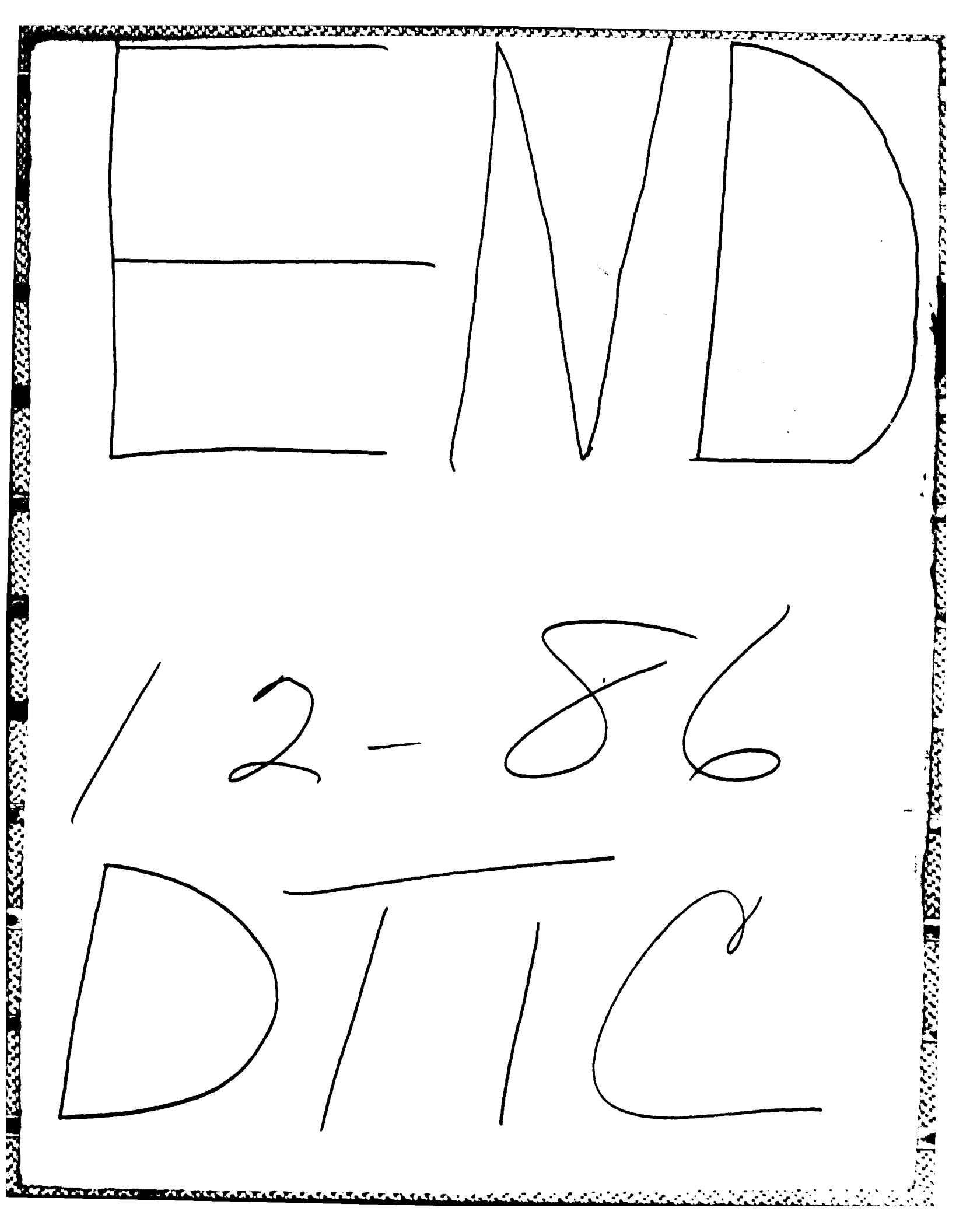
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